The Oxygenation of Iron II Solutions Relationships to Coal Mine Drainage Treatment

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INTRODUCTION

Most coal mine drainage waters, containing sulfuric acid, iron, and aluminum as major impurities, require treatment to reduce the contaminant concentrations to meet recent State regulations prior to their entry into natural waterways. The present, most widely employed treatment process includes neutralization of the waters and subsequent oxidation and precipitation of the iron along with most of the aluminum present. An impurity sludge product is separated for disposal.

Iron occurs in these waters predominantly as the soluble iron (II) ion. Its desired removal as an insoluble hydrated ferric oxide usually involves air oxidation with the associated production of further acid. A knowledge of the oxidation kinetics of the iron (II) ion is of significance in the development of control measures that could prevent formation of these contaminated waters and in providing efficient methods of treatment. In the treatment, the parameters involving this oxidation not only regulate the reaction rate, thus process-equipment design, but also have implications regarding the neutralization reactions and the nature of the resulting sludge.

This paper deals with the oxygenation of iron (II) ions and indicates the relative response of the more important reaction parameters on the measured rates. It is taken from a more extensive study by the authors.[5] The experimental conditions employed were similar to those prevailing in the treatment of mine drainage. The parameters considered were: pH, temperature, iron concentration, and aluminum concentration. Aluminum in mine drainage though commonly considered innocuous as a contaminant, has significant affects during treatment. There are other variables which are not discussed herein such as sulfate concentration and catalytic responses of trace constituents such as copper.

BACKGROUND

The oxygenation of iron (II) ions and the subsequent precipitation of iron (III) can be represented as follows: [1]

$$Fe^{++} + 1/4\ O_2 + 5/2\ H_2O = Fe(OH)_3\downarrow + 2H^+ \qquad (a)$$

This overall reaction involves oxygenation, hydrolysis, and precipitation, of which oxygenation, is believed to be the rate-determining step.[1] Stumm's studies of iron (II) in the pH range 4 to 8 indicate the oxidation rate can be described by the following equation:

$$\frac{-d(Fe(II)^{++})}{dt} = K\ (Fe(II)^{++})\ (O_2)\ (OH^-)^2 \qquad (b)$$

Below pH 3, however, the rate law follows the equation:[2 3]

$$\frac{-d(Fe(II)^{++})}{dt} = K\ (Fe(II)^{++})\ (O_2) \qquad (c)$$

In the pH range 4 to 8, for a given pH and oxygen concentration, the rate expression becomes:

$$\frac{-d(Fe(II)^{++})}{dt} = k' \ (Fe(II)^{++}) \qquad (d)$$

$$\text{where } k' = K \ (OH^-)^2 \ (O_2)$$

which represents a first-order reaction rate.

EXPERIMENTAL

A jacketed reaction chamber was employed in which aeration was achieved by introducing air through a fritted glass disc at the bottom. The gas movement provided violent agitation within the chamber. Glass and calomel electrodes were supported through a stopper at the top of the chamber to lead a signal to a Sargent Recording Titrator, Model D. By proper adjustment of a cam limit switch, the titrating mechanism automatically controlled injection of the alkaline titrant (1.5N NaOH) to maintain a constant pH. A constant temperature bath and pump were employed to circulate water through the glass jacket surrounding chamber to maintain a constant temperature. A schematic representation of the apparatus is shown in Figure 1.

Reactant solutions were prepared with boiled, distilled, deionized water and reagent grade ferrous sulfate heptahydrate, $Fe(SO_4) \cdot 7H_2O$ and hydrated aluminum potassium sulfate, $AlK(SO_4)_2 \cdot 12H_2O$. Reactant solutions were adjusted to pH 2.8 with sulfuric acid prior to addition of the ferrous sulfate salt to insure oxidation would not occur before the experiment was initiated.

Approximately 600 ml of solution were used for each test. The solutions were placed in the reaction chamber and aerated for 30 minutes to ensure saturation of the solution by O_2. The rate of air introduction appeared to maintain this saturated condition since a plot of the pseudo-first order reaction rates conformed to a straight line dependent only upon the decrease in iron (II) concentration. The reaction rate was followed by withdrawing samples at measured time intervals, dowsing them immediately in 2 ml of concentrated HCl and titrating with potassium dichromate solution to determine the concentration of iron (II) ion.

In the initial test series only the pH of the reaction was varied by employing iron solutions (1000 ppm Fe(II)) at 22°C. A second series was conducted at two different levels of the four parameters as a 2^4 factorial experimental design. The variable levels of the second series of tests are given in Table 1.

TABLE 1

VARIABLE LEVELS USED IN RATE STUDIES

Variable	Min	Max
x_1 : pH	5.5	5.7
x_2 : Temp °C	15	25
x_3 : ppm Fe(II)	400	800
x_4 : ppm Al(III)	200	400

The pH values chosen were those which gave reasonably measurable rates by titrimetric techniques. Additional tests were conducted employing an ice bath, which verified the temperature dependence to 5°C.[5] The concentrations of iron and aluminum employed were representative of levels of mine drainage waters in Pennsylvania.

RESULTS

The rates for iron solutions at constant pH were found to conform to a pseudo-first-order reaction as indicated by equation (d). The reaction rate constants, k', are listed in Table 2.

TABLE 2

RATE CONSTANTS FOR OXYGENATION OF IRON $(II)^{++}$ CONSTANT pH

pH	k' $(min^{-1} \times 10^{-5})$
4.50	1.5
4.70	263.
4.75	348.
4.80	517.
5.10	809.
5.18	1190.
5.35	3030.

Iron $(II)^{++}$ = 1000 ppm. T = 22°C

The reaction rate curves (shown in Figure 2) are represented by the following function:

$$\ln (Fe(II)_t) = \ln (Fe(II)_o) - k't \qquad (e)$$

where $Fe(II)_t$ = % Fe(II) remaining at time t (in minutes)

The least-squares-method was used to establish k' values (the slopes of the curves), however, the concentration at t = o was not used due to the bias that would have been created during the initial phase of the reaction while the hydroxyl ion concentration was changing.

There was nearly 2000-fold increase in the reaction rate with a pH increase from 4.50 to 5.35. The change in rate with pH appears to be nearly linear between 4.5 and 5.1 with a very major increase occurring within the next few hundreths of a unit, attaining rates which could not be evaluated by the experimental procedures employed.

The introduction of iron concentration, aluminum concentration, and temperature as additional parameters developed major changes in the reaction rate. Table 3 presents the levels of variables and the calculated rate constants, k', for these tests in the experimental design. With the subsequent observations it is critical to stress that iron (II) ion concentration at t = o was not used to calculate k'. The four reaction rate curves shown in Figure 3 are typical of the plots for all of the tests.

It appears from the curves of these reactions that during the initial phase, i.e. with the introduction of alkali until the particular desired pH was reached, either a different reaction rate or reaction mechanism was taking place than the one plotted for the reaction at a constant pH. The initial rate is much more rapid than that established at constant pH. The curves extrapolate only to 60-85 percent of the known iron (II) concentration at t = o.

During this initial phase, the alkali was injected into the reactant solution at the maximum rate attainable with the equipment (3.5 ml/min). When the desired pH was reached, the minimum injection rate was employed (1/3 ml/min.). The lapsed time for the initial

TABLE 3

LEVELS OF ALL VARIABLES AND RATE CONSTANTS FOR EACH OXIDATION RATE TEST WITH ALUMINUM PRESENT

Test	pH	Temp°C	Fe(II) ppm	Al(III) ppm	k' (min^{-1} x 10^{-5})
E-1	5.5	15	400	200	11.0
E-2	5.7	15	400	200	50.9
E-3	5.5	25	400	200	66.5
E-4	5.7	25	400	200	583.
E-5	5.5	15	800	200	102.
E-6	5.7	15	800	200	1930.
E-7	5.5	25	800	200	1060.
E-8	5.7	25	800	200	6870.
E-9	5.5	15	400	400	5.6
E-10	5.7	15	400	400	31.8
E-11	5.5	25	400	400	23.4
E-12	5.7	25	400	400	239.
E-13	5.5	15	800	400	35.2
E-14	5.7	15	800	400	123.
E-15	5.5	25	800	400	333.
E-16	5.7	25	800	400	1780.

alkali introduction during the multiparameter tests was slightly longer (3-4 min.) than during the pure iron solution tests (2-3 min.).

During the initial rapid injection of alkali, a typically greenish precipitate (assumed to be ferrous hydroxide) was formed at the point of injection, due to the high localized concentration of hydroxyl ions in this region. When no aluminum was present, it appeared that the reaction rate was not appreciable different during this initial phase than after the desired reaction pH was reached.

Thus it seems that the presence of aluminum ions in the reactant solution somehow modifies the oxidation rate of iron (II) in a complex manner. The effect of aluminum hydroxide on the hydrolysis of Fe(II) and Fe(III) has been investigated by Kakabadse and Whinfrey.[4] Their results show that $Al(OH)_3$ changes the rate of precipitation of $Fe(OH)_3$ but does not interfere with $Fe(OH)_2$ precipitation.

The oxidation rate of iron (II) ion continues to increase with pH beyond 5.35 to 5.7 even in the presence of aluminum ions. A 10° temperature increase resulted in a similar change in the oxidation rate by a factor between 3 and 15 times. This temperature dependence was indicated over the temperature range between 5 to 25°C.

The reaction rate constant may appear to vary with the initial iron (II) concentration. However, as the reaction rate for pure iron solution was first-order with respect to iron (II) concentration, the rate constant is independent of the initial iron (II) concentration (see equation d). With interference of $Al(OH)_3$ [2,4] on the hydrolysis rate of iron (III), these changes in the measured rate constant must be attributed to changes in the Fe(II):Al ratio, i.e. the overall oxidation-hydrolysis reaction rate of iron (II) $^{++}$ is proportion to this ratio. Consequently, it was found that a two-fold increase in the Fe(II):Al ratio resulted in increases in the oxidation rate of iron (II) ion between 2 and 40 fold. The effect on reaction rates of aluminum concentration increasing corresponds with a decreasing iron concentration, temperature and pH.

A notable consequence of this study was the observation that the oxidation rate during the initial few minutes of the reaction, while $Fe(OH)_2$ was forming and oxidizing, was extremely rapid and did not appear to be affected by the presence of aluminum, even though the $Al(OH)_3$ precipitate was observed, also, during this period and throughout the test. A proposed explanation is schematically represented as follows:

Hydrolysis Uninhibited by $Al(OH)_3$

$$\begin{tikzcd}[column sep=huge, row sep=large] Fe(II)^{++} \arrow[r, "O_2", "(d)\ \text{Slower}"'] \arrow[d, shift right, "(a)"'] & Fe(III)^{+++} \arrow[d, shift left] \\ Fe(OH)_2 \arrow[r, "O_2", "(b)\ \text{Faster}"'] \arrow[u, shift right] & Fe(III)\downarrow \text{ precipitate} \arrow[u, shift left, "(c)"] \end{tikzcd}$$

Hydrolysis inhibited by interference of $Al(OH)_3$

Reaction (d) in this schematic diagram is slowed due to the inhibition of the hydrolysis reaction (c) caused by the interference of $Al(OH)_3$. Reaction (b), on the other hand, continues at the same relative rate as it would regardless of the presence of aluminum.

Accordingly when aluminum occurs in mine drainage water as a major constituent it is anticipated that reaction rates during treatment will be greatly retarded. If the above proposal is accurate, superior results should result when the waters are completely neutralized and the Fe(II) precipitated as the hydroxide prior to the oxygenation step, i.e. the pH be kept as high as feasible subject to other variables and processes. Further studies are being planned to resolve and quantify these relationships which can result in major changes in process conditions.

ACKNOWLEDGEMENT

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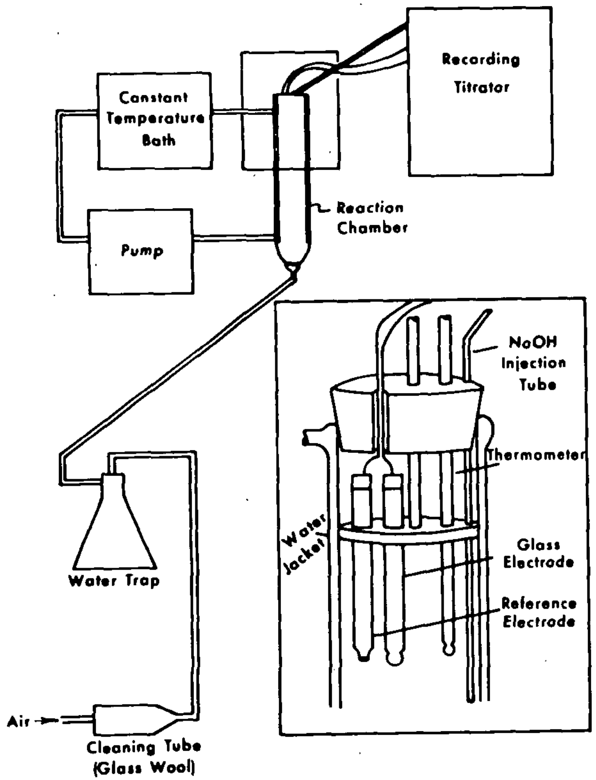

FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS USED IN IRON (II) OXIDATION TESTS

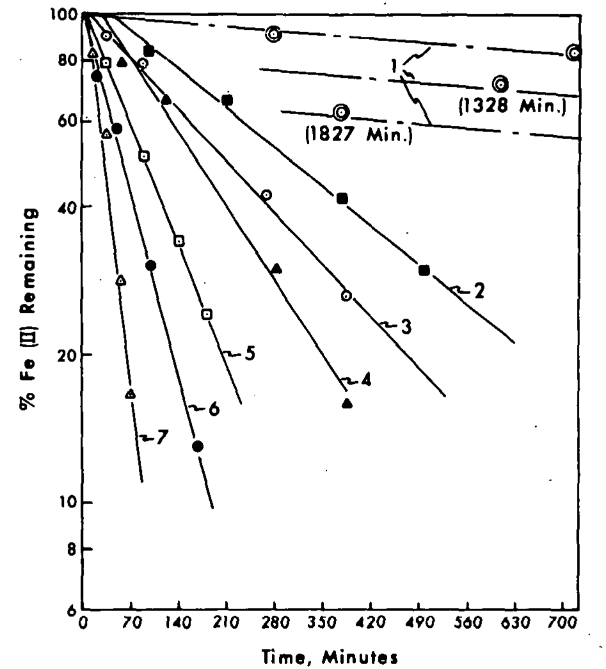

FIGURE 2. OXIDATION RATES OF IRON (II) IN SULFATE SOLUTION AT VARIOUS pH VALUES

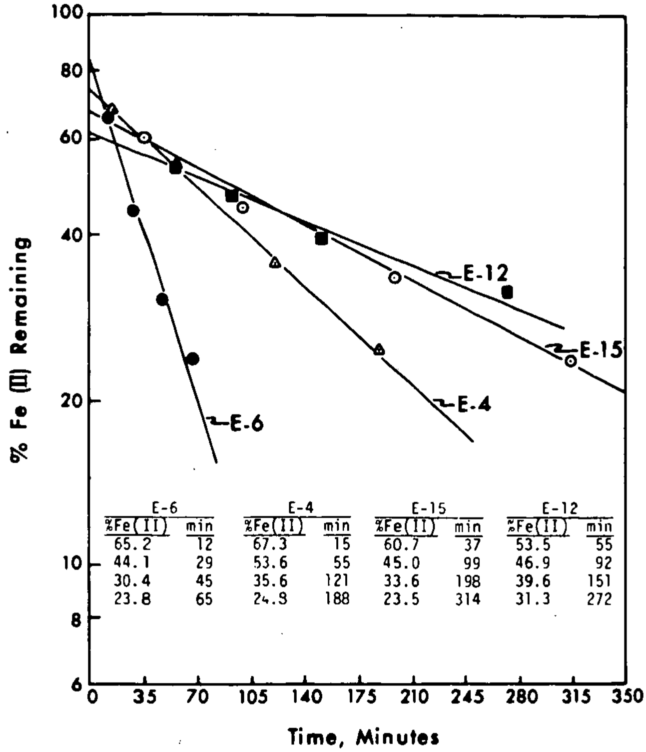

FIGURE 3. EXAMPLES OF OXIDATION RATES OF Fe(II) WITH ALUMINUM PRESENT